

FIBER-REINFORCED

LAMINATES

Rami-Raimund Awad

-and-

Florian Lunzer

PATENT APPLICATION

-with-

Priority of

A 1725/2002 filed -Nov. 15, 2002-

02/069 VAT (11885 * 4)

"Express Mail" mailing label
number ER 573849423

Date of Deposit
- NOVEMBER 12, 2003 -

I hereby certify that this paper or fee is
being deposited with the United States Postal
Service "Express Mail Post Office to
Assess" service under 37 FR 1 10 on the
date indicated above and is addressed to MS PAT

APPLN, Commissioner for Patents,
P.O. Box 1450, Alexandria, VA 22313-1450.

- Amy L. Hamm -

(Typed or printed name of person mailing
paper or fee)

(Signature of person mailing paper or fee)

02/069 VAT

Fiber-reinforced laminates

Field of the Invention

5 The invention relates to fiber-reinforced laminates having at least two layers.

Background of the Invention

10 The production of laminates comprising reinforcing fibers and free-radically or thermally curable polymers has been known. Unsaturated polyesters are normally used for this purpose. These polyesters frequently include relatively large amounts of copolymerizable monomers, customarily styrene, which within the mixture lower the viscosity of
15 the curable mixture and provide good formability, by casting, winding or laying, for example. In the course of processing it is easy for this styrene to escape from the curable compositions owing to the high surface area; such escape causes environmental and occupational hygiene
20 problems.

Summary of the Invention

It is therefore the object of the invention to provide fiber-reinforced laminates and binders therefor which
25 without such addition of styrene produce moldings having smooth, esthetic surfaces and good thermoformability prior to ultimate curing.

This object is achieved through the use of binders, at
30 least of one outer layer, which are curable by irradiation with high-energy light.

The invention accordingly provides fiber-reinforced laminates having at least two layers wherein an outer

layer **A'** containing a polymer **A** containing allyl groups, acrylic groups and/or methacrylic groups and being curable by high-energy radiation and an adjacent layer comprises reinforcing fibers and a curable composition **B'** comprising a polymer **B** selected from systems polymerizable free-radically (**B1**) and by irradiation with high-energy light (**B2**).

The invention further provides a process for producing cured laminates which comprises the steps of (1) producing a cured polymer layer **A'** from a polymer **A** by irradiation with high-energy light and (2) applying a further layer to the layer **A'** produced in step (1), the further layer comprising reinforcing fibers and a curable composition **B'** which originates by free-radical polymerization from a free-radically polymerizable system **B1** and/or by irradiation of a system **B2** with high-energy light.

The invention likewise provides a process for producing shaped laminates which comprises bringing the incompletely cured laminates into the desired shape under the action of heat and pressure and subsequently curing them.

25

Detailed Description of the Preferred Embodiments

In particular, first of all, a molding or a surface of a smooth substrate is coated with a layer **Z** which has an antiadhesive effect, after which in step (1) this layer is coated with a composition comprising a substance **A** polymerizable by irradiation with high-energy light, the substance **A** being polymerized by irradiation and so cured, in step (2) the free surface of this layer is coated with a curable composition **B'** comprising a polymer **B** selected from systems polymerizable free-radically (**B1**)

and by irradiation with high-energy light (**B2**) and reinforcing fibers, and then the curable composition **B'** is at least partly cured, and then detached from the surface or molding for ultimate curing.

5

The polymers **A** and **B2** are selected independently of one another from epoxy acrylates, urethane acrylates, melamine acrylates, polyether acrylates, polyester acrylates, the corresponding methacrylates, and esters of
10 other olefinically unsaturated acids, and polyesters or polyethers both containing allyl groups, and also mixtures thereof.

Epoxy acrylates are reaction products of epoxy resins **C**
15 with carboxyl group-containing olefinically unsaturated compounds **G**. As epoxy resins **C** it is possible to use the glycidyl ethers of dihydroxyaromatics such as resorcinol, dihydroxybenzophenone, dihydroxydiphenylsulfone, and, preferably, bisphenol A and bisphenol F; it is also
20 possible to use glycidyl ethers of aliphatic diols such as butanediol and hexanediol, and also epoxy resins of higher molar mass, which are obtainable preferentially from bisphenol A and/or bisphenol F by the Taffy process (reaction of these bisphenols with epichlorohydrin) and
25 by the so-called advancement reaction (reaction of bisphenol diglycidyl ethers with the free bisphenols). It is also possible to use epoxy resins based on novolaks and epoxidized oils.

30 Carboxyl group-containing olefinically unsaturated compounds **G** which can be used here are in particular acrylic acid and methacrylic acid, but also crotonic acid, vinylacetic acid, and the monoesters of olefinically unsaturated dicarboxylic acids, such as
35 monomethyl maleate, monomethyl fumarate, and the

monoalkyl esters of citraconic, itaconic, and mesaconic acids. Preference is given to the first-mentioned acrylic acid and methacrylic acid.

- 5 Urethane acrylates are reaction products **D(E)F** of polyfunctional isocyanates **D** and hydroxyl group-containing olefinically unsaturated compounds **F** and also, where appropriate, polyfunctional aliphatic alcohols **E**.
- 10 The polyfunctional isocyanates **D** are at least difunctional and can be selected from aromatic and aliphatic linear, cyclic, and branched isocyanates, especially diisocyanates. Preference is given to diisocyanates, where it is possible for up to 5 % of their mass to be replaced
- 15 by isocyanates having a functionality of three or more.

The diisocyanates preferably possess the formula $Q(NCO)_2$, where Q is a hydrocarbon radical having 4 to 40 carbon atoms, in particular 4 to 20 carbon atoms, and preferably

20 an aliphatic hydrocarbon radical having 4 to 12 carbon atoms, a cycloaliphatic hydrocarbon radical having 6 to 15 carbon atoms, an aromatic hydrocarbon radical having 6 to 15 carbon atoms or an araliphatic hydrocarbon radical having 7 to 15 carbon atoms. Examples of such

25 diisocyanates for use with preference are tetramethylene diisocyanate, hexamethylene diisocyanate, dodecamethylene diisocyanate, 1,4-diisocyanatocyclohexane, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (isophorone diisocyanate, IPDI), 4,4'-diisocyanatodicyclohexylmethane,

30 2,2-bis(4-isocyanatocyclohexyl)propane, 1,4-diisocyanatobenzene, 2,4- or 2,6-diisocyanatotoluene and mixtures of these isomers, 4,4'- or 2,4'-diisocyanatodiphenylmethane, 2,2-bis(4-isocyanatophenyl)propane, p-xylylene diisocyanate, and $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-m- or -p-xylylene

35 diisocyanate, and mixtures of these compounds.

In addition to these simple polyisocyanates, also those are suitable which contain heteroatoms in the radical linking the isocyanate groups. Examples of such are polyisocyanates containing carbodiimide groups, allophanate groups, isocyanurate groups, urethane groups, acylated urea groups or biuret groups. For further suitable polyisocyanates reference may be made, for example, to DE-A 29 28 552.

- 10 The polyfunctional aliphatic alcohols **E** used if desired have at least two hydroxyl groups per molecule and 2 to 150 carbon atoms, preferably 3 to 40, and in particular 4 to 20 carbon atoms. They can be linear, branched or cyclic and can also contain heteroatoms, such as ether bonds, ester bonds or secondary or tertiary amine bonds, in the molecule. Compounds of this kind are ether alcohols or polyether alcohols such as polyethylene glycol, polypropylene glycol, mixtures thereof and copolymers and polyoxybutylenediol ("poly-THF"), and also polyester alcohols and amino alcohols. Preference is given to glycol, 1,2- and 1,3-propanediol, 1,2- and 1,4-butanediol, neopentylglycol, 1,6-hexanediol, trimethylolethane, glycerol, trimethylolpropane, erythritol, pentaerythritol, sorbitol, mannitol, ditrimethylolethane, diglycerol, ditrimethylolpropane, diethylene glycol, triethylene glycol, di- and tri-propylene glycol, diethanolamine, N-methyldiethanolamine, triethanolamine, ethoxylated trimethylolpropane, and ethoxylated glycerol.
- 30 Particular preference is given to 1,4-butanediol, and 1,6-hexanediol.

- The hydroxyl group-containing ethylenically unsaturated compounds **F** are aliphatic mono- or polyunsaturated compounds having 3 to 20 carbon atoms and at least one

hydroxyl group. Particular preference is given to allyl alcohol and to the monoesters of dihydric alcohols **F1** with the abovementioned olefinically unsaturated acids **G**, such as hydroxyethyl acrylate, hydroxyethyl methacrylate, 2- and 3-hydroxypropyl (meth)acrylate, 1-hydroxy-2-propyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, and 6-hydroxyhexyl (meth)acrylate, esters of trihydric or higher polyhydric alcohols with an acid containing olefinically unsaturated groups, with at least one hydroxyl group remaining unesterified, examples being trimethylolpropane di(meth)acrylate, pentaerythritol tri(meth)acrylate, and the acrylates and methacrylates formed by reacting (meth)acrylic acid with 1,2-epoxy compounds, in particular with esters or ethers of glycidyl alcohol with monovalent aliphatic alcohols or acids which preferably contain tertiary or quaternary carbon atoms. Examples of such compounds are the ester of glycidyl alcohol with α -branched aliphatic monocarboxylic acids having 5 to 12 carbon atoms.

Melamine acrylates are reaction products of hydroxyl group-containing olefinically unsaturated compounds **F** with alkylolmelamines obtained by reacting melamine and aldehydes, especially formaldehyde. Melamine acrylates are prepared in particular by transesterification of hexamethoxymethylmelamine with the compounds **F**. It is also possible to etherify the compounds **F** directly with methylolated melamine, for example, hexamethylolmelamine; this process, however, is not carried out on the industrial scale.

Polyether acrylates are esters of polyalkylene glycols having degrees of polymerization of preferably from 4 to 100, especially polypropylene glycol, poly(oxy-1,4-butylene) glycol and mixed copolymers having oxyethylene

and oxypropylene units, with the olefinically unsaturated acids specified under **G**; they are normally prepared by transesterification with ethyl (meth)acrylate or similar esters.

5

Polyester acrylates are esterification products of olefinically unsaturated acids **G** with hydroxyl group-containing polyols or polyesters or esterification products of hydroxyl group-containing olefinically unsaturated compounds **F** with acid groups of a polyester. The polyesters are normally derived from linear or branched aliphatic polyols having two or more hydroxyl groups and from 2 to 20 carbon atoms, such as glycol, neopentylglycol, butanediol, 1,6-hexanediol, diethylene and triethylene glycol, trimethylolpropane, pentaerythritol, and sorbitol, and aliphatic linear or cyclic dicarboxylic acids such as adipic acid and cyclohexanedicarboxylic acid, the hydroxyl group-containing polyether polyols based on ethylene oxide and propylene oxide or mixtures thereof and on polytetrahydrofuran, and also on ethoxylated and/or propoxylated polyhydric alcohols, such as those mentioned above.

25 Where "acrylates" are referred to above, in the context of the disclosure these acrylates also of course include the corresponding methacrylates and the esters of the other acids mentioned under **G**.

30 Allyl group-containing compounds are ethers or esters or mixed ether-esters of allyl alcohol with polyhydric alcohols or their ethoxylation and/or propoxylation products or allyl esters of the abovementioned aliphatic carboxyl group-containing polyesters.

35

The unsaturated polyesters **B1** are styrene-free polyesters based on allyl ethers of polyhydric alcohols, the number of allyl groups always being less by one than the number of hydroxyl groups of the unetherified alcohol, aliphatic
5 linear, branched or cyclic diols having 2 to 20 carbon atoms, olefinically unsaturated dicarboxylic acids having 4 to 20 carbon atoms, such as fumaric acid in particular, and small amounts of monohydric alcohols, especially benzyl alcohol, the amount of the latter being such that
10 crosslinking through the polyunsaturated compounds is kept within limits.

Suitable reinforcing fibers are glass fibers in particular but also carbon fibers, aramid fibers, particularly those
15 of the so-called high-modulus polymers such as poly-paraphenyleneterephthalamide (@Kevlar or @Twaron) and copolymers (e.g., @Teijin HM50) containing more than 30 % of units derived from terephthalic acid and para-phenylenediamine, and also fibers of liquid-crystalline
20 polyesters and fibers of ultrahigh molar mass polyethylene (e.g., @Dyneema).

As antiadhesive layer **Z** it is possible to use a standard release agent (for example, waxes, silicone-modified
25 waxes, fatty acid amide waxes, salts of long-chain fatty acids like zinc stearate, polyvinyl alcohol, fluorinated polymers, and natural phospholipids such as soya lecithin).

30 The laminates of the invention can be employed in all applications where use has been made to date, for example, of laminates comprising glass fiber mats with unsaturated polyesters with a gel coat surface.

Examples**Example 1**

Areas of glass coated with soya lecithin as antiadhesive layer were coated with white-pigmented layers of radiation-curable mixtures according to table 1, in film thicknesses of 600, 400, and 200 μm . The coatings were cured by irradiation with UV light (2 gallium-doped mercury lamps and 2 undoped mercury lamps, each with a power of 80 W/cm based on the arc length) at different speeds of travel through the irradiation zone.

Table 1 Composition of the coating materials in g

| Coating | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------------------------|------|------|-----|------|-----|-----|-----|
| unsaturated polyester ¹ | 100 | 50 | 100 | | 100 | 100 | 50 |
| epoxy acrylate ² | | 50 | | | | | 50 |
| urethane acrylate ³ | | | | 100 | | | |
| color paste ⁴ | 10 | 10 | 20 | 20 | 20 | 20 | 20 |
| photoinitiator ⁵ | 4.6 | 4.8 | 5 | 5 | | | |
| photoinitiator ⁶ | | | | | 5 | 4.8 | 5.2 |
| devolatilizer ⁷ | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| reactive diluent ⁸ | 15 | 20 | 25 | 25 | 25 | | |
| reactive diluent ⁹ | | | | | | 20 | 30 |
| viscosity ¹⁰ in mPa·s | 1113 | 1567 | 803 | 1009 | 756 | 841 | 798 |

Key:

- 1 unsaturated polyester (100 %) containing units derived from trimethylolpropane diallyl ether (40 %), benzyl alcohol (5 %), diethylene glycol (15 %), and fumaric acid (40 %), the mass fractions being based on the mass of the polyester
- 2 epoxy acrylate based on a bisphenol A epoxy resin with a weight-average molar mass of approximately 700 g/mol

- 3 urethane acrylate based on aliphatic polyols, an
aliphatic diisocyanate, and a mixture of
hydroxyalkyl (meth)acrylates
- 4 white color paste based on unsaturated polyester,
5 ®Viapal 9010 OEP, Surface Specialties Austria GmbH
- 5 photoinitiator mixture ®Irgacure 184
(hydroxycyclohexyl phenyl ketone) and ®Irgacure 819
(phenyl-2,4,6-trimethylbenzoylphosphine oxide),
equal mass fractions, Ciba Specialty Chemicals
- 10 6 photoinitiator mixture ®Irgacure 184, Ciba Specialty
Chemicals, and ®Lucirin TPO (triphenylphosphine
oxide), BASF AG, equal mass fractions
- 7 devolatilizer ®TEGO Airex 920, Th. Goldschmidt GmbH
- 8 dipropylene glycol diacrylate
- 15 9 triethylene glycol dimethacrylate
- 10 measured in accordance with DIN EN ISO 3219 at 23 °C

After curing at the belt speeds indicated, the irradiated
side of the glass plate was laminated with an unsaturated
20 polyester resin (®Viapal VUP 4782/BEMT 55; Co peroxide
system) reinforced with glass fiber mats, after which the
system was detached from the glass plate. The results
obtained are summarized in table 2.

Table 2 Results

| Coating | Layer thickness Speed | 600 µm | 400 µm | 200 µm |
|---------|--------------------------|--|---|---|
| 1 | 10 m/min | not scratch-resistant, excessive yellowing; surface cracks at 8 m/min | | good degree of cure, structure of the glass fiber mat can be seen, low yellowing |
| 2 | 20 m/min | very hard surface, severe yellowing, excessive contraction after lamination | | good degree of cure, structure of the glass fiber mat can be seen, low yellowing |
| 3 | 10 m/min | inadequate degree of cure, sensitive to scratching, severe yellowing | inadequate degree of cure, sensitive to scratching, structure of the glass fiber mat can be seen, severe yellowing | inadequate degree of cure, sensitive to scratching, structure of the glass fiber mat can be seen, unacceptable yellowing |
| 4 | 12 m/min | good degree of cure, coating film elastic, severe yellowing | good degree of cure, coating film very elastic, severe yellowing | good degree of cure, structure of the glass fiber mat can be seen, unacceptable yellowing |
| 5 | 5 m/min | inadequate degree of cure, sensitive to scratching, no yellowing | good degree of cure, no yellowing | good degree of cure, smooth surface, no yellowing |

| | | | | |
|---|---------|--|---|---|
| 6 | 5 m/min | inadequate degree of cure, coating film remains soft, only partly gelled, no yellowing | inadequate degree of cure, coating film remains very soft, only partly gelled, no yellowing | inadequate degree of cure, coating film is soft, only partly gelled, no yellowing |
| 7 | 8 m/min | good degree of cure, no yellowing, at higher belt speed no through-cure | good degree of cure, no yellowing | good degree of cure, smooth surface, no yellowing |

| | | |
|-------------|-----------------------------------|---|
| Assessment: | degree of cure | good/soft/inadequate = only partial gelling |
| | sensitivity to scratching | insensitive/low/not measurable |
| | visibility of the glass fiber mat | none/slight/severe |
| | yellowing | none/slight/severe |

Example 2

In a second series of experiments UV-curable coatings 2.1 and 2.2 according to table 3 were applied to glass plates as described in example 1 coated with release agent as above. The coatings were cured under 2 mercury lamps and 2 gallium-doped mercury lamps, each with a power of 80 W/cm, at a belt speed of 5 m/min from a distance of 10 cm, and after curing were detached from the glass plates and joined to a UV-curable laminating layer. This layer consisted of a 10 × 20 cm² glass fiber mat (approximately 5 g/m²) to which approximately 20 g of the UV laminating materials 2.3 and 2.4, in accordance with the indication in table 3, have been applied. Following lamination the laminate was cured by irradiation with UV light from the side of the impregnated glass fiber mat. The results are summarized in table 4.

Table 3 UV-curable coating materials (compositions of the coating materials in g)

| Coating material | 2.1 | 2.2 | 2.3 | 2.4 |
|------------------------------------|-----|-----|-----|-----|
| unsaturated polyester ¹ | 100 | 50 | 100 | 50 |
| epoxy acrylate ² | | 50 | | 50 |
| photoinitiator ⁵ | 5 | 5.2 | 5 | 5.2 |
| devolatilizer ⁶ | 0.3 | 0.3 | 0.3 | 0.3 |
| reactive diluent ⁷ | 25 | | 25 | |
| reactive diluent ⁸ | | 30 | | 30 |
| color paste ⁹ | 20 | 20 | | |

For key see table 1

Table 4 Results

| Coating material | Layer thickness | Curing | Yellowing |
|------------------|---|---------------------|--------------|
| 2.1 | 600 μm | good degree of cure | no yellowing |
| | 400 μm | | |
| 2.2 | 600 μm | good degree of cure | no yellowing |
| | 400 μm | | |
| | application rate | | |
| 2.3 | about 20 g to $10 \times 20 \text{ cm}^2$ | good degree of cure | no yellowing |
| 2.4 | about 20 g to $10 \times 20 \text{ cm}^2$ | good degree of cure | no yellowing |

Example 3

In a third series of experiments glass fiber mats ($10 \times 20 \text{ cm}^2$; approximately 5 g/m^2) were applied to wood veneer ($10 \times 20 \text{ cm}^2$) and laminated with UV-curable coatings 3.1 and 3.2 as per table 5 (application rate 20 g/m^2), and cured using 2 mercury lamps each with a power of 80 W/cm at a belt speed of 10 m/min . This procedure gave a veneer/laminate composite in a rational work step, which in the case of a prior art process requires at least two work steps (preparation of the mold, e.g. an aluminum support, and fixing (adhesive bonding) of the veneer on or to the corresponding mold).

This molding (i.e. the veneer/laminate composite) was subsequently coated on the veneer side with a UV clearcoat material in accordance with coating 3.3 (see table 5), the clearcoat material being applied in one instance in 2 coats and in another instance with 3 coats, the wet thickness of each coat being $200 \mu\text{m}$. The coating was cured again by exposure to 2 mercury lamps each with a power of

80 W/cm at a belt speed of 10 m/min. The surface coated with the UV clearcoat material and cured matches a high-build polyester coating that can be completed within a short time. In comparison, for lay-up operations in automobiles (dashboard, steering wheel, gearknob grip) a high-build polyester coating requires at least 6 or 7 applications each at a rate of approximately 250 g/m², possibly with subsequent sanding/polishing/buffing; the overall layer thickness at the end of the processing operation is in that case about 700 to 800 µm; the coating operation takes about 4 to 5 hours, and finishing by sanding and polishing cannot take place until 72 h after the coating operation.

The results are summarized in table 6.

Table 5 UV-curable coating materials (compositions of the coating materials in g)

| Coating material | 3.1 | 3.2 | 3.3 |
|------------------------------------|-----|-----|-----|
| unsaturated polyester ¹ | 100 | 50 | |
| epoxy acrylate ² | | 50 | |
| urethane acrylate ³ | | | 85 |
| photoinitiator ⁶ | 5 | 5.0 | |
| photoinitiator ¹¹ | | | 4.7 |
| devolatilizer ⁶ | 0.3 | 0.3 | 0.3 |
| reactive diluent ⁸ | 25 | | 10 |
| reactive diluent ⁹ | | 30 | |

For key see table 1

Table 6 Results

| Coating material | Layer thickness | Curing |
|------------------|-------------------------------------|---------------------|
| 3.1 | about 20 g to 20×10 cm ² | good degree of cure |
| 3.2 | about 20 g to 20×10 cm ² | good degree of cure |
| 3.3 | 200 µm wet film | good degree of cure |

5
10
15
It is found that styrene-containing unsaturated polyester resins with the conventional free-radical curing by means of cobalt salts and peroxides can be replaced by styrene-free UV-curable systems. The advantage of these systems is the absence of styrene and the increased reactivity of the UV-curable system and consequent higher productivity. Veneer/laminate composites can be produced in one work step using the UV technology. The use of a UV clearcoat system to replace UP coating material produces a distinct increase in productivity owing to more rapid curing.